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Aryl *Bis*(triflates) in Palladium (0) Cross-Coupling Reactions. Synthesis of Polyphenyl-Alkynyl, Alkenyl, and Aryl Ethers

by

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A new *bis*(triflate) monomer was prepared. The *bis*(triflate) was copolymerized with new organostannane comonomers under palladium (0) catalysis. The triflate monomer was also reacted with *bis*(phenol) compounds under basic conditions to afford poly(aryl ethers).

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ARYL *BIS*(TRIFLATES) IN PALLADIUM (0) CROSS-COUPLING REACTIONS. SYNTHESIS OF POLYPHENYL-ALKYNYL, ALKENYL, AND ARYL ETHERS

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Introduction

The synthesis of polymers using a transition metal catalyzed cross-coupling reaction has become a growing and very productive area of polymer chemistry.[1] The use of cross-coupling reactions enables the polymer chemist to prepare sp^2-sp^2, sp-sp^2, and sp^2-sp^3 carbon-carbon under very mild reaction conditions and with excellent functional group tolerance.[2] Polycondensations using a transition metal catalyzed cross-coupling reaction follow polymerization rules governing step-growth processes, and thus, reaction efficiency and monomer purity are critical issues.

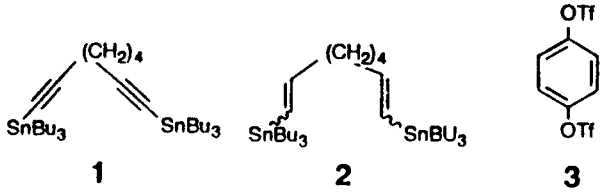
$$X\text{-}R\text{-}X + M\text{-}R^1\text{-}M \xrightarrow[-MX]{\text{Pd or Ni}} \{R\text{-}R^1\}_n$$

X = Halide or Triflate
M = Sn, Mg, Zn, B

As part of our polymer synthesis program we have been exploring the use of palladium (0) catalyzed polycondensation of organostannane and aryl halide partners. Of the cross-coupling reactions developed to date, the organostannane reagents offer the advantages of stability, isolation in analytical pure, and a variety of methods for preparation. Herein we describe the synthesis of new *bis*(trimethylstannyl)- alkynyl and alkenyl monomers, aryl *bis*(triflates), and the use of these new monomers in palladium catalyzed polycondensation reactions.

Results & Discussion

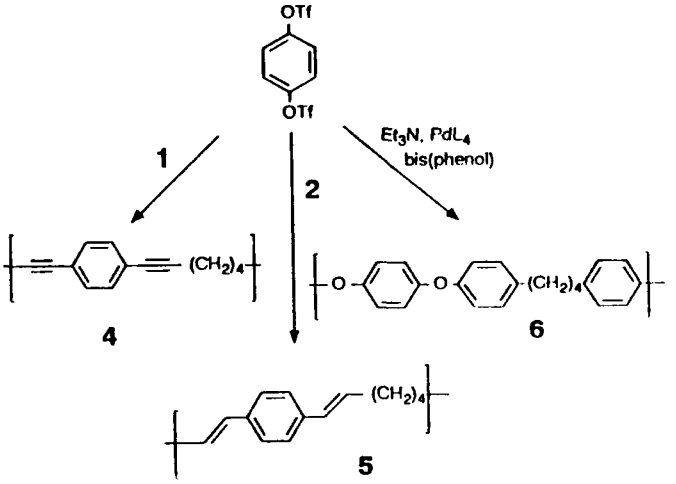
We have prepared three new monomers for use in palladium catalyzed cross-coupling reactions. Monomer 2 is prepared by hydrostannylation of 1,7-octadiyne. Monomer 3 is easily prepared from hydroquinone, triflic anhydride, and polymer-bound 2,6-di-*tert*-butylpyridine.



1 2 3

Polymerization of 3 with comonomer 1 using 1 mol-% $Pd(PPh_3)_4$ (hereafter PdL_4) afforded polymer 4 in 90% yield (Scheme 1). Spectroscopic data is consistent with the proposed structure. GPC data for polymer 4 indicated the average molecular weight to be 8,000. Similar results were obtained by polymerizing 1,7-octadiyne with 3 using PdL_4, CuI, and triethylamine. Polymerization of 3 with comonomer 2 afforded polymer 5 in 95% yield and with an average molecular weight of 7,500. Polymerization of 3 with *bis*(phenol) compounds is found to yield poly(arylethers) of modest molecular weight (M_n ~5000).[3]

Scheme 1



Concluding Remarks

The *bis*(triflate) proves to be an effective monomer in several palladium catalyzed polycondensation reactions. In addition to the direct cross-coupling reactions, carbonylative cross-coupling reactions appear promising with monomer 3.

Acknowledgment. We wish to thank the Office of Naval Research for their generous support of this work.

References and notes

1. The volume of transition metal catalyzed polymerization reactions exploded in the late 80's and continues to grow in the 90's. The reaction type is best cataloged according to metal involved in the transmetalation to palladium or nickel. For the primary development of each cross-coupling reaction see: (organostannanes) Stille, J. K. *Pure Appl. Chem.* **1985**, *57*, 1771; (organoborate) Suzuki, A. *Acc. Chem. Res.* **1982**, *15*, 178; (organozinc) Jabri, N.; Alexakis, A.; Normant, J. F. *Tetrahedron Lett.* **1981**, 959; (organomagnesium) Hayashi, T.; Kumada, M. *Acc. Chem. Res.* **1982**, *15*, 395.

2. For some recent examples see: Perry, R. J.; Turner, S. R. *Polym. Preprints* **1991**, *32(1)*, 335. Percec, V.; Pugh, C.; Cramer, E.; Weiss, R. *Polym. Preprints* **1991**, *32(1)*, 329 and references cited therein. Imai, Y. *Polym. Preprints* **1991**, *32(1)*, 331 and references cited therein. Giesa, R.; Schulz, R. C. *Makromol. Chem.* **1990**, *191*, 857 and references cited therein. Wallow, T. I.; Novak, B. M. *J. Am. Chem. Soc.* **1991**, *113*, 7411.

3. Experimental details to be published elsewhere.